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A comprehensive study on relating cell-wall components of lignocellulosic biomass to oxygenated species formed during pyrolysis

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ABSTRACT

This study was conducted to fundamentally understand the relationship between biomass composition and key pyrolysis oxygenates that affect the quality of bio-oil. Unlike many studies where surrogates are used to probe the effect of biomass characteristics on pyrolysis; in this investigation, we used well-characterized biomass feedstocks with different natural varying levels of plant cell-wall components. With this approach, possible interaction effects of the biomass components which are not revealed in model studies are captured. Selected oxygenates from the pyrolysis of debarked sugar maple, poplar, willow, switchgrass, and hot-water extracted sugar maple were correlated with their composition (namely, glucan, xylan, arabinan, mannan, acetyl, lignin, extractives and ash). The pyrolysis was conducted at 550 °C using a bench scale pyroprobe-GC/MS and Pearson correlation coefficients were used to statistically analyze the data. Quantitatively, relationships between the biomass components and oxygenated species such as acetic acid, levoglucosan, hydroxyacetone, methyl pyruvate, furfural, 2-furanone, 5-hydroxymethyl furfural, 4-allyl-2,6-dimethoxyphenol, coniferyl alcohol, and 2-methoxy-4-vinylphenol were established. Statistically significant correlation between the acetyl content and acetic acid yield indicate that deacetylation of the lignocellulosic cell wall could help in reducing the acidity of bio-oils. Likewise, other strong correlations suggest that carbonyls could be reduced by lowering the hemicellulose fraction. The data also indicated possible interaction between lignin and polysaccharides on the formation of specific oxygenates. For example, it was found that feedstocks with high lignin content tend to produce high yields of hydroxyacetaldehyde. Similarly, feedstocks with high glucan fraction yield more phenolic aldehydes and ketones. Overall, it can be inferred from the results that both genomic science and pretreatment could be used as tools to modify the heterogeneity of lignocellulosics to reduce the complexity of biomass pyrolysis and improve prospects for producing better quality bio-oils.

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1. Introduction

Pyrolysis of biomass produces a liquid intermediate (bio-oil) which could be co-processed with heavy petroleum feedstocks such as atmospheric gas oil (AGO) and vacuum gas oil (VGO) in an existing refinery infrastructure to produce transportation fuels (gasoline, diesel, and jet fuels), heating oil, lubricating oil, and chemicals. However, the raw bio-oil is not useful as a feedstock in the petroleum refinery industry at present. This is mainly due to the poor fuel quality of the raw bio-oil. Typically, the raw bio-oil is heavily oxygenated, corrosive, unstable, viscous, and immiscible with petroleum feedstocks. These undesirable fuel properties are as a result of the several hundreds of reactive oxygenates in the oil. Hence, upgrading technologies such as catalytic cracking and hydroprocessing are used to deoxygenate the bio-oil components (anhydrosugars, carboxylic acids, hydroxyaldehydes, hydroxyketones, and multifunctional phenolics) into hydrocarbons [1,2].

Another attractive strategy to resolve the poor fuel quality of bio-oil is to integrate biomass pretreatment with pyrolysis. As studies show, the physiochemical properties of the raw bio-oil is to a large extent representative of the inherent composition of the biomass even though they can be altered to some extent by process conditions and reactor configuration [3]. The major composition of the secondary cell walls of plants (cellulose, hemicellulose, and lignin) and minor composition (extractives and inorganic matter) all influence the pyrolytic conversion of biomass. Therefore, pre-processing methods could be utilized to modify the plant cell wall composition for thermochemical conversion just as it is being practiced for biochemical conversion. In recent years, pretreatment methods such as hydrothermal/hot-water treatment

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[4–7] and torrefaction [8–13] have been explored in improving biomass pyrolysis. Additionally, genomic science could be utilized to engineer biomass with preferable structural composition to allow selective transformation of biomass into high quality bio-oils. Hence, there is a need to have a good understanding of lignocellulosic chemistry and how the native composition of plant cell wall influences biomass pyrolysis. This would allow pretreatment techniques or plant engineering to be employed more intentionally in addressing issues related to bio-oil fuel quality.

An overwhelming body of research [14–18] has already been conducted on isolated forms of cellulose, xylan, and lignin to elucidate their role in biomass pyrolysis. The effect of inorganic matter has also been well studied [19–21]. Most of the previous studies focused on their thermal behavior, chemical kinetics, decomposition mechanism, degradation products, and influence on the overall biomass pyrolysis product distribution. Nonetheless, their fundamental impact on the formation of bio-oil chemical species such as carboxylic acids and carbonyl compounds which adversely affect the quality of bio-oil is seldom examined closely. Additionally, the use of surrogates does not fully mimic actual biomass behaviors and possible interaction effects of biomass components on the pyrolysis oxygenated species is not revealed, thus limiting the impact of model studies. Furthermore, quantitative influence of the native cell wall composition on the formation of major pyrolysis oil component is rarely studied. A typical example is the case with acetic acid; there is no information on how the degree of acetylation of the cell wall impacts the formation of acetic acid. Another example is in the case of levoglucosan; the effect of cellulose content on its formation is hardly reported. What is commonly known is that; native cellulose in actual biomass forms lower amount of levoglucosan and higher yields of lower molecular weight (LMW) oxygenates whereas isolated pure cellulose produces higher amount of levoglucosan and lower yields of LMW oxygenates. It is therefore important to understand quantitatively, how the relative content of plant cell components correlate with pyrolysis oxygenates. The lack of such information limits useful application of pretreatment or genomic science to selectively remove/modify “causative” precursors in the biomass feedstocks prior to pyrolytic conversion.

The purpose of this investigation is to establish quantitative correlations between biomass cell wall composition and key pyrolysis products. To pursue this goal, lignocellulosic biomass feedstocks with varying cell wall composition were selected for the study. The experimental design utilized the natural varying levels of the cell-wall components in the selected lignocellulosic feedstocks instead of synthetic blends of their isolated forms. Pearson correlation coefficients were used to statistically analyze the data and detect hidden relationships between cell wall composition and pyrolysis products.

2. Materials and methods

2.1. Materials

2.1.1. Biomass feedstocks

In this study, high impact biomass feedstocks including those available in the Northeast U.S. were selected. Sugar maple, debarked sugar maple, willow, switchgrass and hot-water extracted sugar maple were supplied by The State University of New York College of Environmental Science and Forestry (SUNY-ESF). The willow was obtained from clonally propagated biomass willow plantations of ESF and sugar maple samples were obtained from ESF’s Heiberg Forest in Tully, NY. Additionally, hybrid poplar and another willow sample were obtained from Idaho National Laboratory (INL). All samples were dried, ground in a Thomas-Wiley mini-mill (Thomas Scientific), and sized to 60 mesh (250 μm). The moisture content of biomass samples before each test was determined using MJ33 Compact Infrared Moisture Analyzer (Mettler Toledo, Greifensee, Switzerland). Proximate and ultimate analysis of each feedstock shown in Table 1 was performed by Galbraith Analytical Laboratory (Knoxville, TN, USA). Compositional analysis (carbohydrates, lignin, and extractives) in Table 1 was performed by Microbac Laboratories Inc. (Boulder, CO, USA) according to NREL laboratory Analytical Procedures (LAP) [22–24].

2.2. Methods

2.2.1. Thermogravimetric analysis

Biomass samples were first subjected to thermogravimetric analysis in a TA Instruments Q50 TGA. About 5 mg of each biomass sample was heated at 20 °C/min from 25 °C to 750 °C with 60 mL/min of N_2 as a carrier gas.

2.2.2. Biomass preprocessing

Debarked sugar maple was subjected to hot-water extraction (HWE) pretreatment with the goal of inducing selective pyrolysis to minimize the formation of undesirable compounds. The SUNY-ESF HWE process is conducted without the addition of mineral acids/bases at a moderate temperature (160 °C). This pretreatment has been demonstrated to selectively solubilize hemicellulose [10]. Also, water-soluble inorganic earth elements (i.e. K, Ca, Mg and P) present in biomass are also removed by the HWE pretreatment step. In this study, the debarked sugar maple was subjected to HWE at 160 °C for 2 h. Another test was performed at 30 min to evaluate the effect of extraction time. A 4:1 water to biomass ratio was used for the extraction in a 6 L M/K digester with a centrifugal pump for liquor circulation and a PID temperature controller. After extraction, the samples were washed and air dried for storage.

2.2.3. Pyrolysis-GC/MS experiment

The pyrolysis of the various biomass feedstocks were conducted using a CDS Analytical Pyroprobe 5200 (CDS Analytical, PA) interfaced with Agilent 7890A gas chromatograph and 5975C mass spectrometer detector. All experiments were performed in a direct Py-GC/MS mode at atmospheric pressure. In the direct Py-GC/MS mode, the volatiles and gases are immediately and directly transferred to the GC/MS for analysis without trapping. Sample sizes ranging between 0.3 and 0.6 mg were loaded per experiment into a quartz tube reactor of 25 mm in length and 1.9 mm in diameter. The loaded sample in the quartz tube was held in place at the center with small plugs of quartz wool. The quartz tubes were weighed before and after pyrolysis using a Mettler Toledo MS105 semi-micro balance with sensitivity of 0.01 mg (Mettler Toledo, Greifensee, Switzerland). The Pyroprobe control software was programmed to rapidly heat the sample to 550 °C and hold for 20 s. Each experiment was conducted at least five times to ensure reproducibility and accuracy of results. During pyrolysis, the vapors in the pyroprobe zone are swept by ultra-high purity helium carrier gas into the GC/MS for separation and detection. The pyrolysis vapors were separated with a 60 m × 0.25 mm DB-1701 capillary column of 0.25 μm film thickness. The GC inlet was set to 275 °C and a split ratio of 75:1 was used. The column followed a temperature program of 40 °C for 1 min, 6 °C/min to 130 °C, 10 °C/min to 275 °C held for 20 min. Column flow was controlled to maintain a constant linear velocity of 1 mL/min. The ion source and the interface of the mass spectrometer detector were held at 230 °C and 250 °C respectively. Electron ionization of the compounds was performed at 69.9 eV and the ions were separated by their mass-to-charge (m/z) ratios in the range of 28–350. The GC column was calibrated with standards of selected compounds (purchased from Sigma–Aldrich) to allow for quantification and confirmation of peaks present in biomass pyrolysis products. The National Institute

Table 1
Physiochemical characteristics of biomass feedstocks.

Analysis	Biomass feedstocks						
	Hybrid poplar	WILL-I	Willow	Sugar maple with bark	Debarked sugar maple	HWE-sugar maple	Switchgrass
Proximate analysis (wt.% dry basis)							
Volatile matter	86.26	82.70	83.60	84.84	85.56	88.05	79.62
Fixed carbon	12.87	15.41	14.97	14.20	13.63	11.57	19.39
Ash	0.43	1.89	1.43	0.96	0.81	0.38	2.99
Ultimate analysis (wt.% dry basis)							
Carbon	49.07	48.86	49.03	49.10	48.91	49.79	48.02
Hydrogen	5.98	6.02	5.98	5.83	5.87	5.95	5.77
Nitrogen	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Sulfur	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.075
Chlorine	243 ppm	159 ppm	140 ppm	65 ppm	69 ppm	262 ppm	0.30
Oxygen (by difference)	44.49	43.21	43.54	44.11	44.39	43.86	42.85
Compositional analysis (wt.% dry basis)							
Glucan	42.73	–	37.25	–	39.44	48.92	35.85
Xylan	16.2	–	12.58	–	15.91	7.38	22.89
Acetyl	4.25	–	3.16	–	3.76	1.2	2.21
Arabinan	1.76	–	0.72	–	0.23	0	1.98
Mannan	0.11	–	1.41	–	2.27	1.24	0.15
Total lignin	26.14	–	25.32	–	26.33	27.45	23.01
Water extractable others	1.75	–	6.16	–	3.63	5.28	6.16
Ethanol extractives	1.20	–	2.4	–	1.27	5.12	2.48

WILL-I (willow form INL) and HWE-sugar maple (hot-water extracted debarked sugar maple).

of Standards and Technology (NIST) mass spectral library and a custom library created for the mass spectra of the known compounds were both used in the identification of compounds. Analytical standards for the calibration of the GC/MS system were prepared in accordance to ASTM method D4307. For each compound, a linear calibration curve was established for concentrations of 250, 750, 1250, 2500 and 5000 μg/mL. The calibration curves had R^2 value greater than 0.95. Table 2 shows the main pyrolysis products that were quantified and Table S1 shows other major products that were unidentified and unconfirmed in the GC–MS chromatogram of most of the feedstocks.

3. Results and discussion

3.1. Biomass characteristics

The proximate, ultimate, and compositional analyses of the various hardwoods and the herbaceous feedstock used in the study are shown in Table 1. From the proximate analysis, it is clear that the switchgrass contained high amount of inorganic matter compared to the hardwoods. This explains why the fixed carbon (19.39 wt.%) and the ash content (2.99 wt.%) for switchgrass were relatively high. Among the hardwoods, willow (WILL-I) was found to have the

Table 2
Major pyrolysis decomposition products from the selected biomass feedstocks.

Quantified pyrolysis decomposition products	Yield (wt.% dry basis)						
	Hybrid poplar	WILL-I	Willow	Sugar maple with bark	Debarked sugar maple	HWE-sugar maple	Switchgrass
Hydroxyacetaldehyde	11.04	10.74	9.72	9.33	11.76	12.00	7.34
Levoglucosan	6.48	4.31	3.20	3.54	4.45	11.97	2.76
Acetic acid	5.09	4.32	4.32	4.29	4.87	2.26	3.88
Hydroxyacetone	1.27	1.37	1.18	1.06	1.23	0.70	1.38
Methyl pyruvate	1.00	0.87	0.83	0.76	0.97	0.69	0.69
Furfural	0.45	0.40	0.38	0.41	0.44	0.46	0.52
2-Furanone	0.39	0.40	0.35	0.28	0.37	0.21	0.27
5-Hydroxymethyl furfural	0.38	0.38	0.39	0.36	0.43	0.73	0.31
3-Methyl-1,2-cyclopentanedione	0.33	0.36	0.36	0.23	0.39	0.25	0.36
Sinapaldehyde	0.37	BQL	0.17	0.29	0.32	BQL	BQL
4-Allyl-2,6-dimethoxyphenol	0.44	0.30	0.36	0.41	0.44	0.39	0.11
Syringol	0.27	0.23	0.20	0.21	0.24	0.21	0.13
Syringaldehyde	0.26	0.15	0.18	0.22	0.23	0.36	0.04
Trimethoxybenzene	0.22	0.13	0.16	0.20	0.21	0.24	0.05
2-Methoxy-4-vinylphenol	0.21	0.23	0.17	0.18	0.17	0.16	0.69
4-Vinylphenol	BQL	BQL	BQL	BQL	BQL	BQL	0.67
Coniferyl alcohol	0.19	0.58	0.27	0.27	0.29	BQL	0.16
Trans-isoeugenol	0.15	0.12	0.10	0.13	0.12	0.11	0.12
3′,5′-Dimethoxyacetophenone	0.14	0.12	0.12	0.13	0.14	0.09	0.04
Vanillin	0.13	0.10	0.09	0.09	0.10	0.19	0.11
3′,5′-Dimethoxy-4′-hydroxyacetophenone	0.11	0.07	0.08	0.11	0.10	0.14	0.03
Creosol	0.09	0.06	0.06	0.08	0.06	0.10	0.09
Guaiacol	0.07	0.07	0.05	0.06	0.05	0.06	0.12
Eugenol	0.02	BQL	0.01	0.01	BQL	BQL	0.01
Phenol	BQL	0.24	0.08	BQL	0.05	BQL	0.06

WILL-I (willow form INL) and HWE-sugar maple (hot-water extracted debarked sugar maple).

highest fixed carbon (15.41 wt.%) and ash content (1.89 wt.%) due to high inorganic content as well. The hybrid poplar and the HWE-sugar maple on the other hand, had higher amount of volatile matter and very low ash contents. It should be pointed out that, debarking of sugar maple resulted in 15% reduction in ash content. Additionally, HWE pretreatment of sugar maple decreased the ash content by 50% and the fixed carbon by 15%. Even though the proximate analysis indicated key differences between the feedstocks, the results from the organic elemental analysis showed comparable results for carbon, hydrogen, nitrogen and oxygen. The HWE-sugar maple had the highest carbon content (49.79 wt.%), poplar with the highest oxygen content (44.49 wt.%) and switchgrass contained higher amount of sulfur (0.075 wt.%) and chlorine (0.30 wt.%).

Structurally, major differences between the cell wall compositions of the feedstocks were observed as detailed in Table 1. The main components that were determined are glucan, xylan, arabinan, mannan, acetyl, lignin (acid soluble and insoluble lignin), water extractable and ethanol extractives. The glucan content ranged from 35.85 wt.% to 48.92 wt.% and xylan was between 7.38 wt.% and 22.89 wt.%. The acetyl content varied from 1.2 wt.% to 4.25 wt.%. Other hemicellulose polysaccharides such as arabinan and mannan were minor and their amount ranged from as low as 0.11 wt.% to as high as 2.27 wt.%. The lignin content which is the second highest structural component of the biomass feedstocks was between 23.01 wt.% and 27.45 wt.%. It is worth noting that the variation in the distribution of glucan and xylan were larger than lignin among the feedstocks. From the results, the cellulose fraction was lowest in switchgrass and highest in HWE-sugar maple. However, the primary hemicellulose fraction (xylan) was highest in the switchgrass and lowest in HWE-sugar maple. The high amount of xylan determined in the switchgrass can be explained by the fact that, the major hemicellulose unit (glucuronoarabinoxylan) is present in both the primary and secondary cell walls of grasses [25–27]. Hence, xylans are typically high in herbaceous feedstocks. Conversely, hardwood xylans are found mainly in the secondary cell wall and are the dominant noncellulosic polysaccharide[25]. Also, It should be pointed out that the xylans in hardwood are heavily acetylated as evidenced by the high acetyl content of 4.25 wt.% in the hybrid poplar feedstock. Nonetheless, the low amount of xylan (7.38 wt.%) and acetyl groups (1.2 wt.%) found in the HWE-sugar maple was due to selective solubilization of xylan during the hot-water extraction pretreatment. Overall, hybrid poplar and switchgrass had the highest fraction of structural carbohydrates (glucan, xylan, arabinan and mannan) whilst the SUNY-ESF willow had the lowest. With regards to lignin content, the HWE-sugar maple had slightly higher amount, again due to hot-water extraction, but, hybrid poplar had the highest in terms of the natural amount.

Furthermore, the compositional analysis showed that SUNY-ESF willow and switchgrass contained higher amount of soluble non-structural materials compared to hybrid poplar and debarked sugar maple. The water extractables for switchgrass and SUNY-ESF willow were 6.16 wt.%, whereas their ethanol extractives were 2.48 wt.% and 2.4 wt.% respectively. It can be seen that the HWE-sugar maple had comparable high content of extractives as well. However, the high extractives determined in the HWE-sugar could be due to a bias analysis, because, the hot-water extraction pretreatment could induce a change in the solubility of other biomass components [28] and as a result increase the amount of extractable material by water and ethanol. In summary, the proximate, ultimate, and compositional analyses highlighted the chemical differences between the various feedstocks. The differences in the structural components of the feedstocks as observed are in agreement with other compositional analysis reported in the NREL biomass feedstock composition and property database and the literature [29,30].

3.2. Thermogravimetric analysis (TGA)

The TGA and differential thermogravimetric (DTG) curves in Figure S1a and S1b respectively supports the biomass characteristics discussed in the previous section. Observation of the TG curves, show that switchgrass forms high amount of residue (20.4%) compared to poplar and sugar maple (13.6%) at 550 °C. This observation is a characteristic of their ash content and is in agreement with the proximate analysis. It implies that, poplar and debarked sugar maple feedstocks will produce higher liquid yield and less char during pyrolysis.

The DTG curves on the other hand complement the compositional analysis results. It can be seen that the maximum rate of decomposition between 300 and 400 °C which is attributed to cellulose was highest in poplar and lowest in switchgrass. Also, the maximum rate of decomposition between 250 and 300 °C which is attributed to hemicellulose was found to be highest in switchgrass and lowest in willow. Furthermore, the shoulder at 210 °C which could be due to decomposition of non-structural components in biomass was relatively high in willow and switchgrass compared to poplar and sugar maple. Pretreated samples of sugar maple were also analyzed and the result is shown in Figure S2. The DTG curve confirms the removal of hemicellulose upon HWE pretreatment as was reported in compositional analysis. Consequently, the extracted samples showed relatively high fraction of cellulose with highest rate of decomposition around 375 °C. The sugar maple sample that was subjected to HWE pretreatment for 2 h showed a much strong effect and the hemicellulose fraction seem to be significantly removed.

3.3. Analytical pyrolysis of various biomass feedstocks

Biomass pyrolysis generates a complex mixture of over hundred different oxygenates. In this study, the yields of major decomposition products that were detected by the GCMS from the pyrolysis of the selected hardwoods and switchgrass are presented in Table 2. Calibration curves of their pure form were used for the quantification. The major oxygenated species identified include hydroxyacetaldehyde, acetic acid, levoglucosan, hydroxyacetone, methyl pyruvate, furfural, 2-furanone, 5-hydroxymethyl furfural, 4-allyl-2,6-dimethoxyphenol, coniferyl alcohol, and 2-methoxy-4-vinylphenol (Fig. 1A).

The graph in Fig. 1B is a plot of carbon yields versus molar O/C ratios of the major oxygenated species from debarked sugar maple. It can be seen clearly that hydroxyacetaldehyde which has very high molar O/C ratio accounted for 9.61% of the biomass carbon. This shows hydroxyacetaldehyde as the highest single bio-oil component produced that contributes significantly to the oxygenated nature of pyrolysis oil. Other compounds with equally high O/C ratios such as acetic acid, levoglucosan, and hydroxyacetone were produced in reasonable amounts as well. They accounted respectively, 4.16%, 4.04% and 1.01% of the biomass carbon. Conversely, the yields of other species such as 2-methoxy-4-vinylphenol, guaiacol, furfural, and 5-HMF which were found to contribute less to the oxygenated nature of bio-oil were rather low in yields. The results confirm that highly oxygenated specifies which are corrosive (e.g. acetic acids) and unstable (e.g. hydroxyacetaldehyde) are present in significant quantities in bio-oils thus negatively impacting its fuel properties.

The results in Table 2 show that the yields of the above mentioned bio-oil components are to some extent dependent on the type of biomass. For example, switchgrass produced 20% less acetic acid, 37% less hydroxyacetaldehyde, 12% more hydroxyacetone, and 75% more 2-methoxy-4-vinylphenol when compared to the debarked sugar maple. Also, hybrid poplar formed 50% more levoglucosan, 20% more methyl pyruvate and 10% more

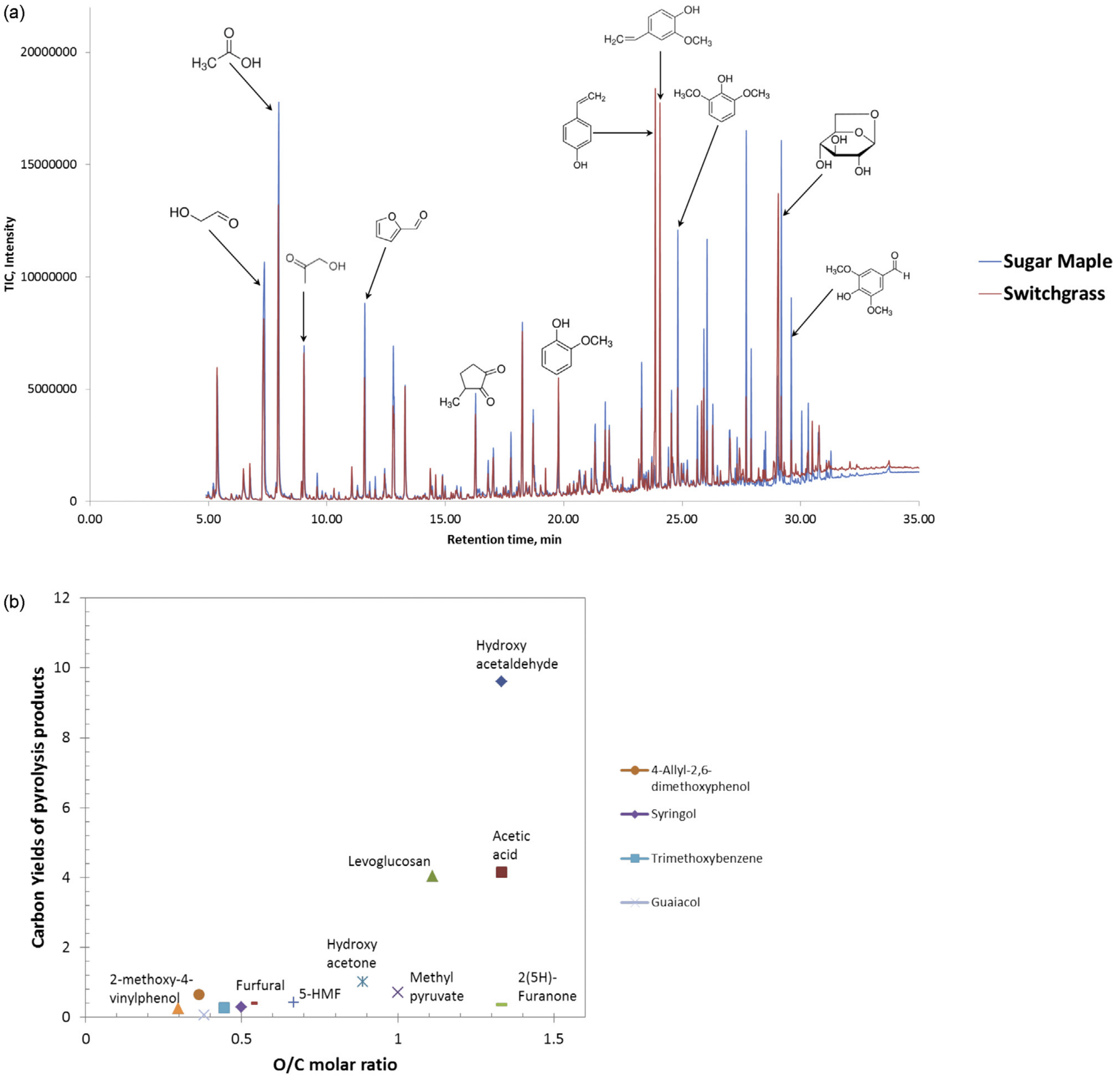

Fig. 1. (A) GC/MS chromatograms of eluted products from pyrolysis of sugar maple and switchgrass and (B) a plot of carbon yields versus O/C molar ratio showing the role of individual compounds from the sugar maple on the oxygenated nature pyrolysis oil.

hydroxyacetaldehyde than willow. Furthermore, the HWE-sugar maple had the highest yield for both hydroxyacetaldehyde and levoglucosan but the lowest yield for acetic acid. These variations in yields are due to differences in cell wall composition of the selected biomass feedstocks. Hence, an attempt was made in this study to identify relationships if any, between the structural components of the biomass feedstocks and the formation of oxygenate compounds that are detrimental to the quality of bio-oil.

3.4. Relating pyrolysis oxygenated species and plant cell wall components

Although the source of some of the oxygenates are generally known from model studies, it is difficult to discern the interactive effects of major plant cell wall constituents on the formation of bio-oil chemical species during pyrolysis. For this reason, Pearson correlation was performed to identify significant (*P* value <0.05) relationships between the cell wall components of biomass and selected pyrolysis products. The Pearson correlation coefficients which are similar to classical linear correlation coefficients were computed using XLSTAT package. The Pearson correlation coefficients and the *P*-values are presented in Tables 3 and 4 respectively.

3.4.1. Effect on carboxylic acids

The main carboxylic acids that contribute directly to the total acid number (TAN) of pyrolysis oils are formic, acetic, propionic and glycolic [31]. Acetic acid (HAc) is the highest single acid produced during pyrolysis and is believed to be formed as a result of hemicellulose degradation [31–35]. Cellulose degradation is also reported to contribute to the yield of HAc [36,37]. However, there is no data at present that demonstrates the association of hemicellulose or cellulose with the formation of carboxylic acids. Also, it is unclear in the literature whether HAc formation is dependent

Table 3
Pearson correlation matrix.

Variables	Ash	WE	EE	Lignin	Glucan	Xylan	Arabinan	Mannan	Acetyl	Glucan and xylan
HAA	**−0.962**	−0.544	0.149	**0.978**	0.751	−0.754	−0.728	0.553	0.133	−0.097
HAc	0.019	−0.565	**−0.991**	−0.241	−0.588	0.535	0.428	−0.016	**0.970**	−0.008
LG	−0.683	−0.184	0.724	0.779	**0.991**	−0.765	−0.513	0.050	−0.506	0.224
HA	0.695	−0.066	−0.765	−0.842	−0.866	**0.963**	0.799	−0.397	0.516	0.256
MP	−0.504	−0.832	−0.806	0.301	−0.100	0.088	0.049	0.205	**0.944**	−0.006
FF	0.319	−0.242	−0.023	−0.371	0.065	0.569	0.626	−0.698	−0.149	**0.965**
5HMF	−0.692	−0.028	0.770	0.837	**0.937**	**−0.881**	−0.740	0.321	−0.549	−0.029
2-Furanone	−0.184	−0.585	**−0.923**	−0.026	−0.460	0.294	0.223	0.146	**0.985**	−0.199
MCP	0.442	−0.046	−0.843	−0.541	**−0.885**	0.682	0.299	0.216	0.664	−0.201
TMB	**−0.996**	−0.581	0.150	**0.982**	0.778	−0.785	−0.644	0.429	0.167	−0.107
SYG	**−0.976**	−0.683	−0.071	**0.923**	0.630	−0.659	−0.580	0.472	0.373	−0.123
DMPP	**−0.950**	−0.648	−0.137	**0.885**	0.534	−0.653	−0.570	0.502	0.445	−0.248
SYGA	**−0.937**	−0.399	0.439	**0.981**	**0.922**	**−0.882**	−0.682	0.341	−0.133	−0.053
VA	−0.478	−0.079	0.786	0.582	**0.930**	−0.606	−0.332	−0.151	−0.637	0.382
DMAC	**−0.962**	−0.458	0.366	**0.989**	**0.896**	−0.860	−0.671	0.357	−0.054	−0.056

Values in bold are different from 0 with a significance level alpha = 0.05.
WE = water extractives, EE = ethanol extractives, HAA = hydroxyacetaldehyde, HAc = acetic acid, LG = levoglucosan, HA = hydroxyacetone, MP = methyl pyruvate, FF = furfural, 5HMF = 5 hydroxymethyl furfural, MCP = 2-metyl-1,3-cyclopentanedione, TMB = trimethoxybenzene, SYG = syringol, DMPP = 4-allyl-2,6-dimethoxyphenol, SYGA = syringaldehyde, VA = vanillin, and DMAC = 3,5-dimethoxy-4-hydroxycinnamaldehyde.

on the amount of xylan/mannan or on the degree of acetylation of the biomass feedstock. In this study, the results in Fig. 2A and Table 3 clearly show a statistically significant correlation between the yield of HAc and the acetyl content in the various biomass feedstocks. The correlation coefficient was 0.97 with a *P*-value of 0.006. Conversely, the correlation coefficients between the yield of HAc and other carbohydrates such as xylan (0.53), glucan (−0.58), and arabinan (0.43) were all statistically insignificant. Hence, the results provide evidence that acetyl groups are the main precursor of HAc in biomass pyrolysis.

Nevertheless, it should be pointed out that even though xylan and arabinan demonstrate weak correlations with HAc formation, at an alpha level of 0.05, they could be potential sources as well. The cellulose fraction on the other hand does not seem to contribute to a large extent on HAc formation because of the observed negative correlation. Another compound that had significant correlation with acetyl content was a methyl pyruvate (MP) as shown in Fig. 2B. This carboxylic acid derivative had a correlation coefficient of 0.94 and a *P*-value of 0.016. It is also noteworthy that biomass feedstocks with high ethanol extractives (EE) formed less HAc and methyl pyruvate. The correlation between HAc and EE was −0.991 and that of MP with EE was −0.81. These observations could be attributed to the fact that such feedstocks contain lower acetyl groups.

In a broader perspective, it means that the amount of acids found in pyrolysis oil can be considerably reduced by using biomass feedstocks that are less acetylated. *O*-Acetylation occurs on the backbone of many cell polymers especially in the hemicellulose fraction. The degree of acetylation varies between lignocellulosic feedstocks such as woody, herbaceous, and agricultural residues. The hardwoods primarily consist of *O*-acetyl-(4-*O*-methylglucurono)-xylan, softwoods are made-up of *O*-acetyl-galactoglucomannan and grasses mainly consist of glucuronoarabinoxylan [25,27,38]. Typically, the *O*-acetyl-(4-*O*-methylglucurono)-xylan in hardwoods is highly acetylated. The hardwood xylan backbone contain about 9–14% of the acetyl group, which corresponds to a degree of substitution of 0.36–0.54 [38]. Additionally, its xylose residues on average have seven *O*-acetyl groups and one 4-O-methylglucuronic acid linked (1 → 2) per 10 xylose units [26,39]. Conversely, in softwoods, the *O*-acetyl-galactoglucomannan is less acetylated (1 acetyl groups per 3–4 backbone units). In addition to acetyl groups found in hemicellulose, the lignin monolignols are also acetylated. It has been reported to be linked to the gamma-carbon of the aliphatic side chain and predominantly on the syringyl units in lignin [40]. For hardwood xylem, lignin acetylation could be up to 50% (w/w) [41]. This suggests that, pyrolysis oils produced from softwoods could be less

Table 4
P-values at significance α level of 0.05.

Variables	Ash	WE	EE	Lignin	Glucan	Xylan	Arabinan	Mannan	Acetyl	Glucan and xylan
HAA	**0.009**	0.344	0.810	**0.004**	0.144	0.141	0.163	0.334	0.831	0.877
HAc	0.976	0.321	**0.001**	0.697	0.297	0.352	0.473	0.980	**0.006**	0.990
LG	0.204	0.767	0.166	0.121	**0.001**	0.131	0.377	0.937	0.384	0.717
HA	0.193	0.916	0.132	0.074	0.057	**0.008**	0.105	0.508	0.374	0.678
MP	0.386	0.081	0.099	0.622	0.873	0.889	0.937	0.741	**0.016**	0.992
FF	0.600	0.695	0.971	0.538	0.917	0.317	0.258	0.190	0.811	**0.008**
5HMF	0.196	0.964	0.128	0.077	**0.019**	**0.048**	0.153	0.599	0.338	0.963
2-Furanone	0.767	0.300	**0.025**	0.967	0.435	0.631	0.718	0.815	**0.002**	0.749
MCP	0.456	0.941	0.073	0.347	**0.046**	0.204	0.625	0.727	0.222	0.746
TMB	**0.000**	0.305	0.810	**0.003**	0.121	0.115	0.241	0.471	0.788	0.864
SYG	**0.004**	0.204	0.910	**0.025**	0.255	0.226	0.305	0.422	0.536	0.843
DMPP	**0.013**	0.237	0.827	**0.046**	0.354	0.232	0.316	0.389	0.453	0.687
SYGA	**0.019**	0.506	0.459	**0.003**	**0.026**	**0.048**	0.205	0.574	0.832	0.933
VA	0.415	0.900	0.115	0.303	**0.022**	0.279	0.585	0.808	0.248	0.525
DMAC	**0.009**	0.438	0.545	**0.001**	**0.040**	0.061	0.215	0.555	0.932	0.929

Values in bold are different from 0 with a significance level alpha = 0.05.
WE = water extractives, EE = ethanol extractives, HAA = hydroxyacetaldehyde, HAc = acetic acid, LG = levoglucosan, HA = hydroxyacetone, MP = methyl pyruvate, FF = furfural, 5HMF = 5 hydroxymethyl furfural, MCP = 2-metyl-1,3-cyclopentanedione, TMB = trimethoxybenzene, SYG = syringol, DMPP = 4-allyl-2,6-dimethoxyphenol, SYGA = Syringaldehyde, VA = vanillin, and DMAC = 3,5-dimethoxy-4-hydroxycinnamaldehyde.

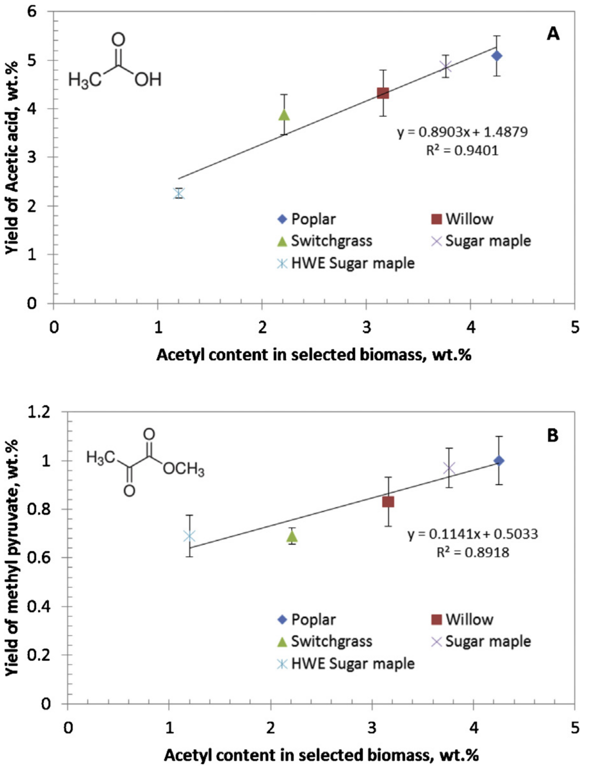

Fig. 2. (A) Correlations between the yield of HAc and acetyl content and (B) correlation between the yield of MP and the acetyl contents in the selected biomass feedstocks.

acidic than those from hardwoods. Furthermore, pyrolysis oils from herbaceous feedstocks would probably contain much less acids since their hemicellulose fraction (glucuronoarabinoxylan) has relatively lower degree of acetylation [42]. As an example, Greenhalf et al. [43] performed a comparative study with various feedstocks and in their work, pyrolysis oils produced from beech wood was relatively more acidic with a pH of 2.86 compared with the bio-oil from miscanthus grass which had a pH of 3.78. Likewise, in the present investigation, the sugar maple wood formed produced 4.9 wt.% of HAc, but upon HWE treatment, the HAc yield decreased to 2.26 wt.%. This is because, the pretreatment promoted deacetylation. Therefore, it can be inferred from the results that reducing the degree of acetylation among cell wall components by either pretreatment or plant engineering will be very useful in overcoming the corrosive nature associated with pyrolysis oils from lignocellulosic feedstocks.

3.4.2. *Effect on aldehydes*

The main types of aldehydes quantified were linear (hydroxyacetaldehyde), furanic (furfural and 5-HMF) and phenolic (sinapaldehyde and vanillin). Most of the aldehydes with the exception of the phenolic type have been reported to originate from the holocellulose portion of biomass [44]. With respect to hydroxyacetaldehyde (HAA), it has been established that its formation is by ring cleavage of the cellulose monomer with subsequent rearrangement of the two-carbon fragments. It should also be mentioned that other studies have documented the formation of HAA from hemicellulose [18,45]. In this study, the results from the hardwood feedstocks and switchgrass showed that none of the native holocellulose component significantly correlated very well with the yield of HAA (Table 3). The strongest positive correlation (0.751) was with glucan, whereas the correlation with xylan was negative. Despite the fact they are statistically insignificant at an alpha level of 0.05, the data shows to some extent that HAA is primarily produced from cellulose (Fig. 3A). Hence, it can be suggested that xylan (or hemicellulose) contributes less to the formation of HAA.

Importantly, the lack of significant quantitative relationship between HAA and glucan could be attributed to potential interaction effect from other biomass components. As it can be seen from Table 3 and Fig. 3B and C, lignin and ash content had significant positive and negative correlation coefficients with HAA respectively. The observed relationship between ash content and HAA (Fig. 3B) in this study is different from some model studies which suggest that inorganic ions typically enhance the fragmentation of cellulose into lower molecular weight compounds such as HAA [20,36,46,47]. Nonetheless, other studies have equally shown that inorganic compounds such as $MgCl_2$ $CaCl_2$, $Ca(NO_3)_2$, and $CaHPO_4$ could in fact can decrease the yield of HAA [46,48] which seem to be in agreement with the observation made in this study. At the moment, the effect of ash on HAA is unclear and raises more questions about the influence of the inherent inorganic matter on biomass pyrolysis. Another important factor that appears to have influenced the formation of HAA is the potential interaction effect between lignin and polysaccharide. In this study, a significant correlation (0.978) between lignin and HAA (Fig. 3C) observed suggests such effect. This provides further evidence about possible interactions between the cell wall components of lignocellulosics during biomass pyrolysis.

The formation of 5-hydroxymethyl-furfural (5-HMF) on the other hand correlated well with the glucan content (Fig. 3D). The correlation coefficient of 0.937 was statistically significant. The yield of 5-HMF ranged from 0.3 to 0.7 wt.% and biomass feedstocks with higher glucan content generally forming relatively higher amount of 5-HMF. The highest yield of 0.67 wt.% was from the HWE-sugar maple sample which had a glucan content of about 49 wt.%. It can be inferred from the empirical results that 5-HMF is a direct product of cellulose degradation. This is in agreement with studies on cellulose pyrolysis that suggest 5-HMF is produced competitively from ring-opening and rearrangement reactions of cellulose [17,37].

In the case of furfural (FF), there were no significant interactions between glucan, xylan, lignin or other cell wall components. However, a stronger but statistically insignificant correlation (0.857) is seen when you consider both glucan and xylan (Fig. 3E). In spite of the fact that the polysaccharides appeared to be the source of furfural, the correlation suggests that FF is not a primary product of their decomposition. Previous studies points to the fact that FF is a degradation product of levoglucosan and 5HMF.

3.4.3. *Effect on ketones*

The yields of the confirmed ketones in this study were below 1.5 wt.%. The yield of hydroxyacetone (HA) and 2-furanone (FN) correlate very well with the monomeric units of hemicellulose. On the other hand, the yield of 2-methyl-1,3-cyclopentanedione (MCP) had a strong relationship with glucan. HA was the most abundant hydroxyketone produced and the yield ranged between 0.7 and 1.46 wt.%. The correlation between HA and xylan was significant ($P \leq 0.08$) with coefficient of 0.922 and an R^2 of 0.93 (Fig. 4A). Additionally, HA had a strong positive relationship with arabinan (0.800) and a negative correlation with glucan (−0.866). Hence, the findings indicate that the formation of HA from biomass pyrolysis is to a large extent influenced by the xylan content. As an example, switchgrass produced the highest HA yield as a result of its high xylan content (22.9 wt.%) and HWE sugar maple formed the lowest yield (0.81 wt.%) due to lower xylan content (7.38 wt.%). The relationship between ash content and the yield of HA was found to be positive but statistically insignificant within the limits of the observed data.

The formation of 2-furanone on the other hand had a significant positive correlation coefficient (0.985) with acetyl content. Fig. 4B shows a good relationship between the yield of 2-furanone

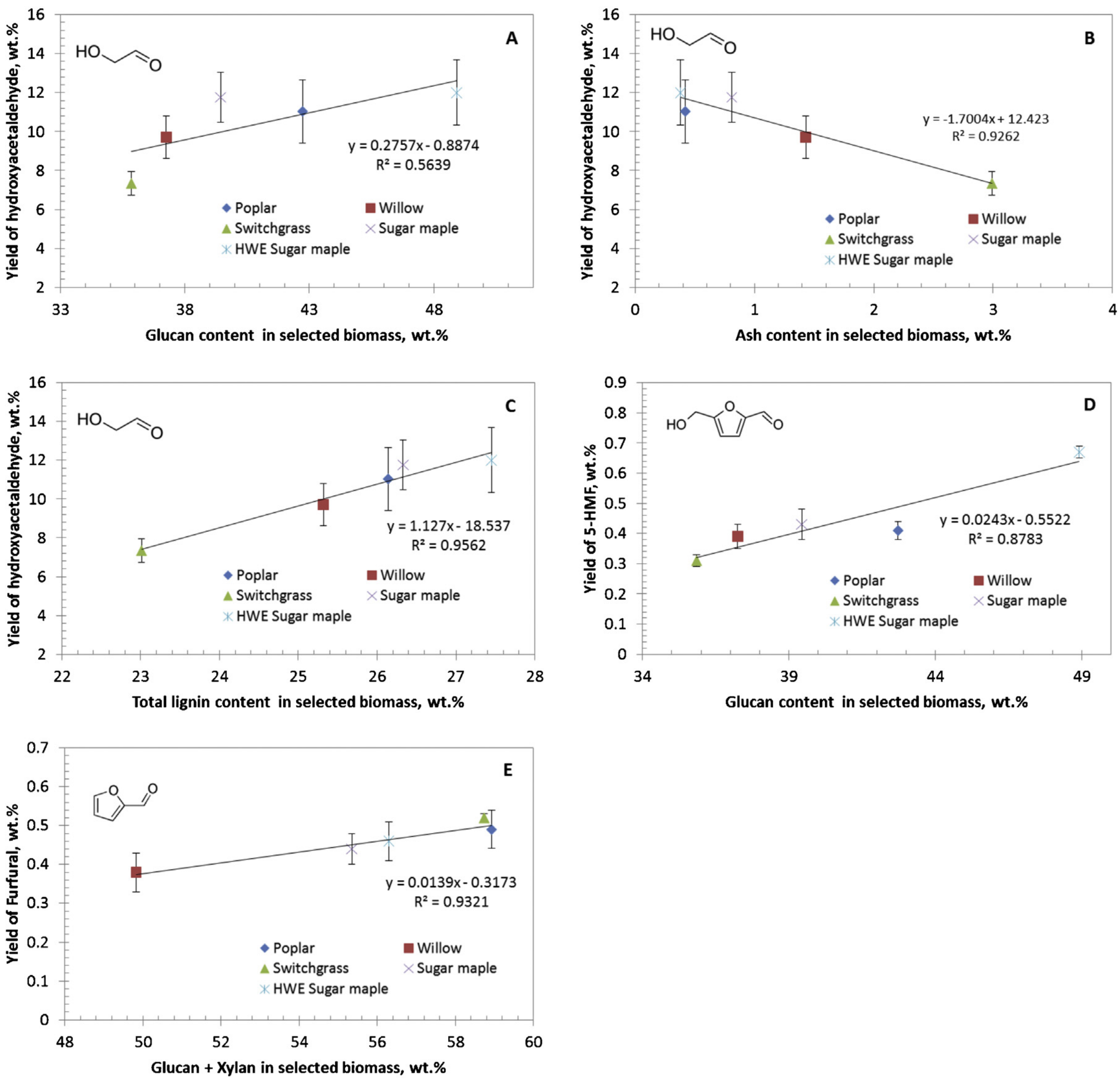

Fig. 3. Correlation plots: (A) HAA versus glucan content, (B) HAA versus ash content, (C) HAA versus lignin content, (D) 5-HMF versus glucan content, and (E) FF versus glucan + xylan content.

and acetyl content. This suggests that biomass feedstocks with high acetyl groups tend to form more of 2-furanone. Likewise, the yield of 2-metyl-1,3-cyclopentanedione(MCP) had a statistically significant ($P \leq 0.046$) negative correlation coefficient (−0.885) with glucan as shown in Fig. 4C. There was a positive correlation coefficient (0.682) with xylan but it was insignificant. The results indicate that high cellulose fraction impairs the formation of MCP whiles high xylan content increases its yield. Nonetheless, the source of 2-furanone and 2-methyl-1,3-cyclopentanedione was not obvious.

3.4.4. *Effect on anhydrosugars*

Levoglucosan (LG) is the major anhydrosugar derivative that is produced from biomass pyrolysis. For pure cellulose pyrolysis, yields close to 60 wt.% of LG can be produced [49,50]. However, the native cellulose in lignocellulosic biomass forms significantly lower yields of LG. In this study, the yield of levoglucosan from pyrolysis of the selected feedstocks ranged between 2.76 wt.% and 11.97 wt.%. Notably, it can be seen from Fig. 4D, the yield of LG correlated very well with glucan content. It had a significant correlation coefficient of 0.991 ($P \leq 0.001$) and R^2 value of 0.98. The formation of LG in particular is known to be a direct product from depolymerization of cellulose polymer [44,49,50]. It has also been shown that the presence of mineral matter affects the pyrolytic degradation of cellulose and it explains why a lower yield of LG is produced from actual biomass [36,47]. The results also showed that the relationship between the ash content and the yield of LG was negative even though the correlation coefficient was statistically insignificant. Thus, the data affirms the notion that inorganic matter could have negative effect on LG formation. As an example, hot-water extraction of sugar maple reduced its ash content by 53% and consequently resulted in a threefold increase in the formation of LG. Incidentally, considering all the selected feedstocks, it appears that the effect of naturally occurring alkali and alkaline earth metals on the native cellulose in formation of LG is subtle when compared to the effect seen with isolated pure cellulose [50]. Thus, it can be inferred from the results that the yield of LG from biomass pyrolysis to a large extent is directly proportional to the actual amount of cellulose presents in the biomass. Based on the graph in Fig. 4D, a biomass feedstock with 50 wt.% cellulose fraction and without any pretreatment would yield about 12.3 wt.% of LG. Nonetheless, it should be emphasized that the nature and amount of the inorganic matter as well as the degree of polymerization/crystallinity of the cellulose are influential factors that affect LG production [46,49]. For future studies, it would be important to decouple the

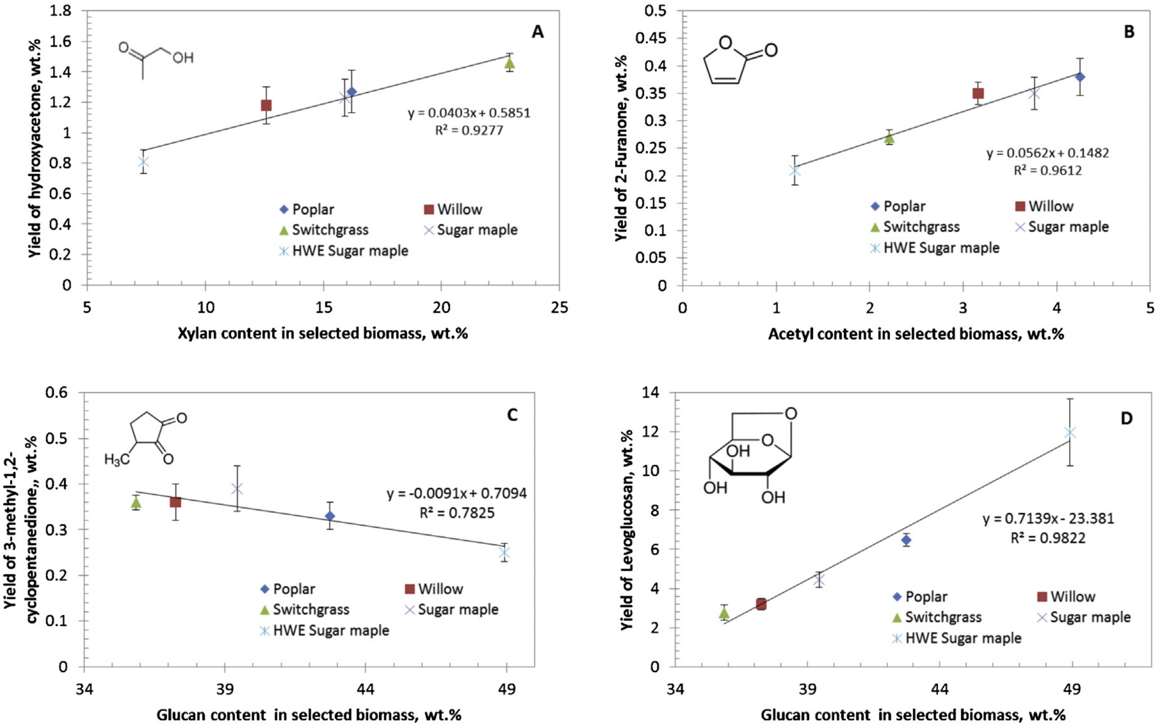

Fig. 4. Correlation plots: (A) HA versus xylan content, (B) 2-Furanone versus acetyl content, (C) MCP versus glucan content, and (D) LG versus glucan content.

individual main effects of cellulose content and natural occurring alkali and alkaline earth metals on the formation of LG as it pertains to actual biomass and not isolated cellulose.

3.4.5. *Effect on multifunctional phenolics*

The phenolics quantified in this study revealed the key difference between the switchgrass lignin and the hardwood lignins. Hardwood lignin is composed of both guaiacyl and syringyl units [51] whilst lignin in herbaceous feedstocks contains coumaryl units in addition to both guaiacyl and syringyl [52]. As shown by the results, the switchgrass produced exclusively 4-vinylphenol (0.67 wt.%) and relatively high yields of 2-methoxy-4-vinylphenol (0.69 wt.%), and guaiacol (0.12 wt%). On the contrary, the hardwood formed relatively high yields of syringyl derivatives. The predominant compounds include 4-allyl-2,6-dimethoxyphenol, syringaldehyde, 3,5-dimethoxy-4-hydroxycinnamaldehyde, and syringol. The presences of guaiacyl derivatives were minimal and they include creosol, isoeugenol and coniferyl alcohol. It should be mentioned that, the high yields of 4-vinylphenol and 2-methoxy-4-vinylphenol seen in the pyrolysis products of switchgrass could also be enhanced by the esterified nature of lignin-carbohydrate complex in herbaceous feedstocks with both ferulic and *p*-coumaric acids [25,53,54]. Thus, during pyrolysis, the ferulate and the *p*-coumarate esters could undergo decarboxylation to yield vinyl phenolics.

As expected, a number of the lignin degradation products had strong relationship with the total lignin content (See Fig. 5). 4-allyl-2,6-dimethoxyphenol ($P \leq 0.046$), syringaldehyde ($P \leq 0.003$), trimethoxybenze ($P \leq 0.003$), syringol ($P \leq 0.025$), and 3′,5′-dimethoxy-4′-hydroxyacetophenone ($P \leq 0.001$) demonstrated significant correlation with lignin content. The interesting finding is the relationship between glucan content and the formation of phenolics aldehydes and ketone. As shown in Table 3, syringaldehyde (0.981), vanillin (0.930) and 3′,5′-dimethoxy-4′-hydroxyacetophenone (0.896) had significant correlation coefficients with glucan. The results indicate that feedstocks with high cellulose fraction produce relatively high quantities of phenolics with carbonyl substituents. Additionally, it was found that feedstocks with high ash content produce lower yield of multifunctional phenolics according to the results. Once again, it can be inferred from the results that intrinsic interaction among the components of plant cell wall, especially between cellulose and lignin do occur during pyrolysis of actual biomass.

3.5. *The impact of biomass composition on pyrolysis oil quality in a broader context*

The nature of lignocellulosic biomass presents a fundamental challenge to the production of high quality pyrolysis oil. As it can be seen from the results in this investigation, the cell wall composition of biomass directly influence the molecular makeup of the resulting pyrolysis oil. Likewise, the chemistry of pyrolysis oil reflects its fuel properties. In order to leverage existing petroleum-refining infrastructure to produce various fuel grades in the near term, the raw bio-oil must be within certain standard fuel specifications. Subject to compliance with these specifications, the stabilized bio-oil can be introduced into the refinery at different streams; i.e. at the front end (atmospheric and vacuum distillation) or midstream (reforming, fluid catalytic cracking (FCC), hydrotreating, and hydrocracking). A study by Mercader et al. [55] showed that bio-oils with oxygen content as high as 28 wt.% could be co-processed successfully with FCC feed. Agblevor et al. [56] also demonstrated that biocrude oils with oxygen content of 20–25% can be co-cracked with standard gas oil [56]. These previous studies suggest that the pyrolysis oil need not be completely deoxygenated before it can be used as a refinery feed. It is well known that bio-oil as a refinery feedstock should be non-corrosive, stable and have a reasonable API (American Petroleum Institute) gravity. Besides, it is believed that reduction in acidity to acceptable levels and significant improvement on the oil stability are also critical to facilitate the introduction of raw bio-oil into existing petroleum refineries.

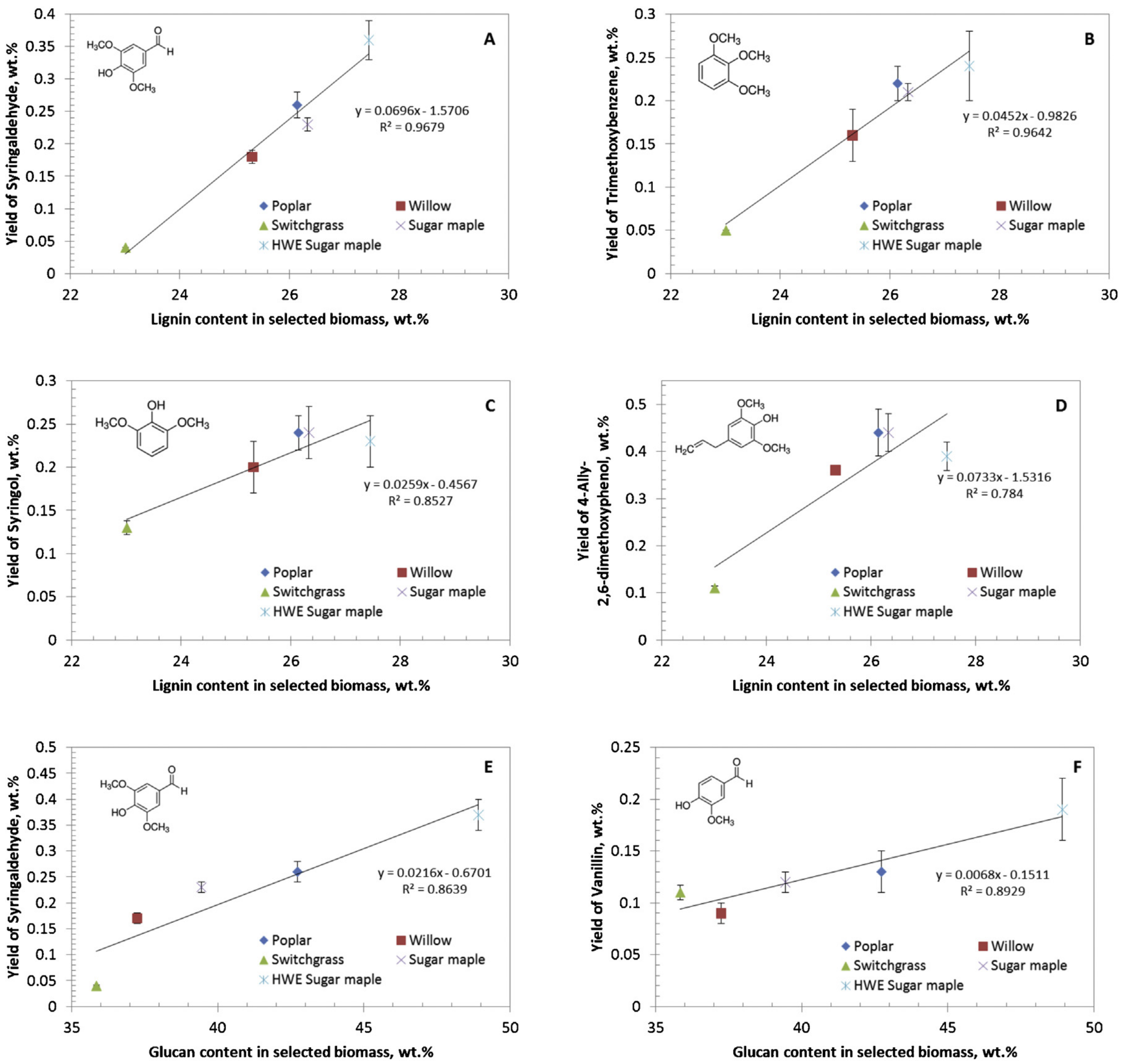

Fig. 5. Correlation plots: (A) SYGA versus lignin content, (B) TMB versus lignin content, (C) SYG versus glucan content, (D) DMPP versus lignin content, (E) SYGA versus glucan content, and (F) VA versus glucan content.

Preprocessing of biomass, such as the HWE evaluated here, or genetic manipulation, such as that offered by clonal propagation of biomass willow, offer opportunities to modify the plant cell wall composition/structure to improve bio-oil quality. The ideal biomass should be able to form a lower yield of potential organic destabilizers and undesirable components upon pyrolytic breakdown. Therefore the first group of undesirable oxygenates that need to be considerably inhibited during pyrolysis are carboxylic acids since their presence render the bio-oil corrosive [57] and also catalyze aldol condensation reactions during storage [58]. Keiser and co-workers [59] at Oak Ridge National laboratory demonstrated that the acidity of bio-oil contributes corrosion and stress cracking in mild and low alloy steels. To increase the acceptance of bio-oil in existing petro-refinery infrastructure, TAN which is typically between 60 and 110 for raw bio-oil from woody biomass [31] would have to be reduced to less than 5. In refinery operations, crude oils with a TAN higher than 0.5 are considered acidic [60]. Oasmaa and co-workers at VTT found that the total amount of acids in pyrolysis oil correlates with the TAN [31]. Their results indicated that an oil with about 5 wt.% of acids would result in a TAN close to 80. This demonstrates quantitatively the effect of organic acids on the acidity of pyrolysis oil. It is also worth mentioning that post-pyrolysis removal of the carboxylic acids could be challenging; they are difficult to convert with mild hydrotreatment [61–63] and in some cases with catalytic pyrolysis [45,64–66]. Nonetheless, extensive hydroprocessing which involves high levels of external hydrogen and pressure have been shown to reduce the TAN of bio-oil to less than 3 [63]. It is therefore conceivable that preventing the formation of acidic compounds during pyrolysis would be advantageous. It would lower the TAN number as well as minimize the extent of downstream hydrotreatment/stabilization processes. The results from this study, establishes that the yield of HAc can be reduced by decreasing the degree of acetylation in biomass. Deacetylation of biomass feedstocks can either be achieved by pretreatment or possibly by genetic engineering or a manipulation such as clonal selection in willow. The wide range of HAc content in the materials studied implies that important variation exists in nature and manipulating acid content may be possible. Hot-water extraction of biomass is an example of pretreatment that can be used to induce cleavage of the bonded acetyl ester groups in the plant cell wall. The added advantage of this treatment is that the over 50% of the acetyl groups are removed could be recovered with other removed acid and organic components as a commodity chemicals for sale to generate revenue.

The second class of potential destabilizers that would have to be minimized during pyrolysis is hydroxycarbonyls (e.g. aldehydes and its derivatives). The carbonyls in the raw bio-oil are reactive oxygenated species and they are responsible for polymerization/condensation reactions leading to formation of higher molecular weight compounds [58,67]. Oasmaa et al. [68] have shown that the amount of aldehydes and ketones in pyrolysis oil decrease during storage as a result of their consumption in reactions that form water-insoluble compounds. Based on the results from this work, the utilization of feedstock preprocessing/modification as a way to inhibit the formation of carbonyls during pyrolysis would be challenging since the carbonyls does not seem to be produced exclusively from a particular component of the cell wall. The linear and furanic carbonyls are generated from the holocellulose portion and the aromatic carbonyls are formed from the lignin component of the biomass. Hydroxyacetaldehyde, being the predominant aldehyde showed high correlation with cellulose content while the major ketone, hydroxyacetone, is largely produced from xylan. Additionally, 5-HMF is more of a decomposition product of cellulose and furfural is a product from both cellulose and hemicellulose. These are just a few of the carbonyls in pyrolysis oils and it can be seen that there is no simple route to prevent their formation unlike HAc. A plausible approach to decrease the overall amount of carbonyl compounds may be to use feedstocks with higher lignin content and lower hemicellulose content. Research at SUNY-ESF has shown that it is much easier to remove the hemicellulose fraction by HWE pretreatment than cellulose [27]. Also, among the three major components of the plant cell wall, hemicellulose appears to be the most complex of all with respect to its heterogeneous mixture of monosaccharides. Hence, its removal could reduce the complex nature of biomass pyrolysis bio-oils. It consist of D-xylose, D-mannose, D-glucose, D-galactose, L-arabinose, L-rhamnose, 4-*O*-methyl-D-glucuronic acid, D-glucuronic acid, and D-galacturonic acid [25,38]. Hemicellulose accounts for 25–35% of the mass of dry wood, 28% in softwoods, and 35% in hardwoods [69]. Cellulose on the other hand is simple and well defined, it is only a linear polymer composed of D-glucose subunits linked by β-glycosidic bonds [38]. Thermochemically, the hemicellulose is the most reactive polymer in the lignocellulosic feedstocks; it degrades quickly during pyrolysis between 200 and 300 °C with maximum decomposition at 260 °C. Moreover, it is the major source of carboxylic acids in bio-oil. Furthermore, studies on pyrolysis of xylan and galactoglucomannan in a fluidized reactor suggests that hemicellulose decomposes less into organic products but it rather forms more water, char and gas [35]. Therefore, considering all the reasons above, it is appears that lignocellulosic biomass with lower hemicellulose content and higher fractions of lignin and cellulose can potentially result in the production of relatively stable bio-oils.

The formation of higher molecular weight (HMW) compounds would have to be reduced to improve upon the viscosity of the bio-oil. In general, the viscosity of bio-oil is related to the molecular weight and not the functionality of the oxygenated species per se. Most of the HMW compounds produced during pyrolysis are from the lignin fraction of the biomass. As it can be seen from the results in Table 2, most of the phenolics with the exception of phenol, guaiacol, 4-vinylphenol and creosol have higher molecular masses. To increase the formation of lower molecular weight (LMW) phenolics, the lignin would have to be made up of LMW monolignols units as well. The molecular mass of the three monolignols of lignin increase in the following order: sinapyl alcohol » coniferyl alcohol > *p*-coumaryl alcohol. Hence, a biomass feedstock containing lignin which is exclusively made up of paracoumaryl would most likely breakdown into phenolics of lower molecular weight. To support this, the results showed that the switchgrass lignin produced exclusively higher yields of 4-vinylphenol, 2-methoxy-4-vinylphenol and guaiacol than the hardwood feedstocks which gave high yields of syringyl derivatives such as 4-allyl-2,6-dimethoxyphenol. In comparison, the molecular mass of 4-allyl-2,6-dimethoxyphenol is 37.5% more than that of 4-vinylphenol. The reason why switchgrass lignin produced phenolics of relatively lower MW is because it contains more of paracoumaryl units compared to the hardwood feedstocks. Hence, it is desirable that dedicated energy crops be engineered or selected to constitute primarily such monolignols. It is worth mentioning that other HMW oxygenates of holocellulose origin such as anhydrosugars, pyrans and furans could contribute to higher viscosity of the pyrolysis products.

Lastly, it can be inferred from the plot of carbon yields versus molar O/C in Fig. 1B that the use of feedstocks with higher lignin content could reduce the overall oxygen content of the bio-oil. The results show that lignin decomposition products have lower molar O/C ratios. In contrast, the carbohydrate decomposition products such as hydroxyacetaldehyde, levoglucosan, and acetic acid have very high molar O/C ratios and thus contribute significantly to the oxygenated nature of pyrolysis oil. Hence, preprocessing biomass feedstocks or engineering plants to have higher lignin content would be desirable in terms of lowering the oxygen content of the bio-oil. Nevertheless, such plant feedstocks would consequentially produce lower yields of bio-oil and higher yields of bio-char. Therefore, further studies would have to be conducted to demonstrate any beneficial effects of high lignin feedstocks and also determine if the tradeoffs are worthwhile. Overall, engineering plants to contain higher content of components such as oil (e.g. resins or oleoresin) and waxes would lead to the formation of bio-oil with lower oxygen content.

4. Conclusion

The overall goal of this investigation is to correlate the native cell-wall components of biomass on the yield of oxygenated species that limit pyrolysis oil applications. The findings from the study provide guidance for the production of non-corrosive stable bio-oils by selecting or designing plants for sustainable energy plantations of the future and inclusion of an HWE preprocessing step. The results suggest that the formation of carboxylic acids (HAc in particular) can be reduced by deacetylation of the lignocellulosic cell wall. Hydroxycarbonyls could be reduced by using feedstocks with high lignin and cellulose fractions. Finally, it is preferable for the lignin to be rich in paracoumary alcohol monolignols.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jaap.2014.05.016.

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